

ON THE MECHANISM OF AVALANCHE-LIKE CRYSTALLIZATION OF EPSOMITE

È. D. Rogacheva, A. A. Rosenblum, A. V. Belyustin

1969

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196901.54730>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Figure 1: distribution curves of the chirality index of epsomite crystals

Figure 1: Figure 1: distribution curves of the chirality index of epsomite crystals

Abstract

Full Text

UDC 548.52

CRYSTALLOGRAPHY

E. D. ROGACHEVA, A. A. ROZENBLYUM, A. V. BELIUSTIN

ON THE MECHANISM OF AVALANCHE-LIKE CRYSTALLIZATION OF EPSOMITE

(Presented by Academician A. V. Shubnikov, 20 XII 1968)

In paper (¹) the distribution curves of the occurrence of right- and left-handed crystals of magnesium sulfate heptahydrate (epsomite) during crystallization from solution under various conditions were presented and discussed. It was also suggested there that, at supersaturations of 130-250 g/l, crystallization in closed crystallizers proceeds with a decisive participation of the mechanism of crystal multiplication.

Subsequently, additional experiments were carried out for the indicated supersaturations. Crystallization was conducted in closed Petri dishes; the volume of solution was 50 ml. In Fig. 1A (curve 1) a refined experimental distribution of the chirality index $k =$

Fig. 1. Distribution curves of the chirality index of epsomite crystals. **1** — experimental curves (**A** — supersaturation 130-250 g/l, solution volume 50 ml; **B** — supersaturation 250-300 g/l, solution volume 500 ml); **2** — theoretical curves (**A** — $a = 2$, $P_d = 1/3$, $P_l = 1/3$; **B** — $a = 8$, $P_d = P_l = 1/2$)

$$= n_d / (n_l + n_d),$$

where n_d is the number of right-handed crystals and n_l is the number of left-handed crystals in the precipitate. As is evident from the figure, for supersaturations of 130-250 g/l a cup-shaped asymmetric form of the curve is characteristic. The asymmetry of the curve is explained by the fact that, along with dissymmetric extraneous particles, left-handed crystallization centers participate in nucleation.

The next series of experiments had the aim of creating such crystallization conditions as would ensure deactivation of the left-handed centers while preserving

some activity of the symmetric centers. This aim was achieved when crystallizing a solution with a supersaturation of 250–300 g/l under slow cooling. Crystallization was conducted in round flasks of 0.5 l capacity, which were cooled in air after the solution had been held at a temperature 5–7° above the saturation point. Greater preliminary superheating leads to complete deactivation of impurities, and crys-

crystals do not form. Under the indicated conditions the crystallizability of the solutions was about 30%. A symmetric distribution of the transparency index was obtained (Fig. 1B, curve 1). A characteristic and somewhat unexpected feature of the curve is the maximum in the middle.

To explain the form of the occurrence-distribution curves, the notion of crystallization as the result of the superposition of two processes was used: heterogeneous nucleation of crystals and their multiplication. To construct a mathematical model of the process it was necessary to observe the course of crystallization and obtain some additional data.

In general outline the process proceeds as follows. At some moment in time the first crystallite appears at the bottom of the flask. Then new crystallites arise, usually separated from one another. The total number of primary crystals varied from experiment to experiment but, as a rule, did not exceed 20. The growth of the crystallites, at first calm and slow, then accelerates in the direction of the z axis and leads to the formation of defective, often subdivided ends of the crystals. At some moment t_1 , needle-like offshoots form on one of the crystallites at various angles to the z axis. After this, in the region of the concentration flux above the crystal, the finest needles appear; as they grow, they sink and fall to the bottom. Soon a considerable number of needles of different sizes accumulates around the crystal. Gradually other crystals also enter into the process of needle-like multiplication,* though not necessarily all of them. Many of them remain passive in the sense of multiplication. In each experiment the number of active (parent) crystals was counted. Their average number $\bar{n}$ proved to be 2.97. By the time the last active crystal enters the process, the number of needles in the volume increases greatly. This moment t_2 is noted as the end of the activation period $\tau = t_2 - t_1$. Then avalanche formation takes place. The volume of the solution is filled with the finest crystallites, and the solution becomes turbid. Simultaneously with the filling of the solution by the emerging crystals, the grown crystals settle, and the thickness of the sediment increases. The end of the avalanche-formation period t_3 is noted by the clarification of the upper layer of the solution. The duration of this period $\tau_1 = t_3 - t_2$ is somewhat shorter than the activation period. The mean value of τ_1/τ was found to be 0.88.

Fig. 2. Distribution of the number of parent crystals. *a*—experimental distribution ($\bar{n} = 2.97$), *b*—theoretical distribution ($a = 3$).

For a mathematical description of the process it is essential that the experimental distribution of the number of active crystals is similar to the Poisson

Fig. 2. Distribution of the number of parent crystals. a —experimental distribution ($\bar{n} = 2.97$); b —theoretical distribution ($a = 3$).

Figure 2: Fig. 2. Distribution of the number of parent crystals. a —experimental distribution ($\bar{n} = 2.97$); b —theoretical distribution ($a = 3$).

distribution (Fig. 2). Since during the activation period the supersaturation of the solution decreases only slightly and the parent crystals are, as a rule, separated from one another, the activation of the parent crystals may be regarded as a collection of rare independent events obeying Poisson's law. Since experiments in which crystallization is absent are not taken into account, the conditional probability of the appearance of n parent crystals should be used, on the assumption that $n \geq 1$:

$$P_n = \frac{e^{-a} a^n}{(1 - e^{-a})n!} = \frac{1}{e^a - 1} \frac{a^n}{n!}. \quad (1)$$

* Needle-like multiplication of epsomite was also observed in work ⁽²⁾.

The parameter a can be estimated from the relation $\bar{n} = a/(1 - e^{-a})$. Each of the active crystals may be right-handed with probability P_d , or left-handed with probability P_l . To describe the first series of experiments (the asymmetric case) it was assumed that $P_d = 1/3$, $P_l = 2/3$. This choice of probabilities was justified by the fact that the mean handedness index of epsomite under the given conditions is 0.35. For the symmetric case $P_d = P_l = 1/2$.

If there are n parent crystals, 2^n different combinations of right- and left-handed crystals successively entering into propagation are possible. For the symmetric case, the probability of each combination is $(1/2)^n$. For the asymmetric case the corresponding probability will be $(1/3)^s (2/3)^{n-s}$, where s is the number of right-handed crystals in the combination. Let us denote the probability of occurrence of each combination of n active crystals in the symmetric case by q_n , and in the asymmetric case by r_{sn} . Taking (1) into account, these probabilities are equal to:

$$q_n = \frac{1}{2^n} P_n = \frac{1}{e^a - 1} \frac{a^n}{2^n n!}, \quad (2)$$

$$r_{sn} = (1/3)^s (2/3)^{n-s} P_n = \frac{1}{e^a - 1} (1/3)^s (2/3)^{n-s} \frac{a^n}{n!}. \quad (3)$$

The propagation law for an individual crystal cannot be established by direct observations. It can be formulated only on the basis of certain general considerations. The propagation process is avalanche-like, i.e., it is accompanied by a rapid increase in the number of crystals. We assume that the law of crystal

propagation is exponential: $N(t) = e^{\alpha(t-\theta)}$, where $N(t)$ is the number of crystals formed by time t , θ is the time of activation of the parent crystal, and α is a certain constant.

Let us consider the case in which n parent crystals arise. We assume that the moments of their activation, arranged in increasing order $0 \leq \theta_1 \leq \dots \leq \theta_m \leq \dots \leq \theta_n \leq \tau$, are equiprobable in the interval τ . In other words, the system of random variables $(\theta_1, \theta_2, \dots, \theta_n)$ is uniformly distributed in an n -dimensional cube with edge τ . The mean number of crystals formed from a parent crystal that began to propagate at time θ_m is expressed as follows:

$$N_{mn} = \frac{n!}{\tau^n} \int_0^\tau \int_{\theta_1}^\tau \dots \int_{\theta_{n-1}}^\tau e^{\alpha(\tau-\theta_m+\tau_1)} d\theta_1 d\theta_2 \dots d\theta_n. \quad (4)$$

The appearance of the factor $n!$ before the integral is explained by the fact that there are $n!$ ways of placing n crystals at the fixed times $\theta_1, \theta_2, \theta_3, \dots, \theta_n$. If the change of variables $\alpha\theta_1 = x_1, \alpha\theta_2 = x_2, \dots, \alpha\theta_n = x_n$ is made, then formula (4) takes the form (taking into account that $\tau_1 = 0.88\tau$):

$$N_{mn} = \frac{n!e^{1.88\gamma}}{\gamma^n} \int_0^\gamma \int_{x_1}^\gamma \dots \int_{x_{n-1}}^\gamma e^{-x_m} dx_1 dx_2 \dots dx_n, \quad (5)$$

where $\gamma = \alpha\tau$.

To estimate the value of γ , one should calculate the mean number of crystals formed from one parent crystal, assuming that the activation time θ is random and uniformly distributed in the interval from 0 to τ . This number is equal to

$$\frac{1}{\tau} \int_0^\tau e^{\alpha(\tau-\theta+\tau_1)} d\theta = \frac{e^{1.88\gamma}(1-e^{-\gamma})}{\gamma}.$$

The mean number of crystals formed from n parent crystals will be n times larger. On the other hand, this number can be found from the formula

(5) as the sum N_{mn} for $m = 1, 2, \dots, n$. Both methods of calculation give the same result

$$\sum_{m=1}^n N_{mn} = \frac{ne^{1.88\gamma}(1-e^{-\gamma})}{\gamma}. \quad (6)$$

In practice, the total number of crystals in the precipitate does not, on average, depend on n and is of the order of 10^4 . From the estimate $ne^{1.88\gamma}(1-e^{-\gamma})/\gamma \simeq 10^4$, for n varying from 1 to 10, a value of γ from 6 to 5 is obtained; i.e., as the number of parent crystals increases, the activation period is somewhat shortened.

The theoretical occurrence-distribution curve was constructed as follows. For each combination of parent crystals (with n from 1 to 8), k was calculated to an accuracy of 0.01. For each value of k , the probability was determined from (2) or (3). For example, for $n = 4$, for the combination $llld$, the quantity $k_{llld} = (N_{14} + N_{44}) / (N_{14} + N_{24} + N_{34} + N_{44})$, and its probability in the symmetric case is

$$q_n = \frac{1}{2^4} \frac{1}{e^a - 1} \frac{a^4}{4!}.$$

The values of the right-handedness coefficients were divided into 20 intervals, each of width 0.05. The probabilities that the value of k falls into a given interval were summed. The theoretical curve constructed in this way for the dissymmetric case at $a = 2$ reproduces the experimental one well (Fig. 1A, curve 2). For the symmetric case, at small a , the theoretical curves have a cup-shaped form. As the parameter a increases, the bottom of the cup rises, and at $a \geq 8$ a clearly expressed maximum appears in its middle. In Fig. 1B, the theoretical curve (2), obtained for $a = 8$, is shown. Curves 1 and 2 are similar in character, although the experimental curve corresponds to $\bar{n} = 2.97$, i.e., to $a = 3$, and not to 8. Apparently this can be explained by the fact that exact accounting of the number of active crystals is difficult, especially when the number of primary crystals is large and the distance between them is small. This accounting is also complicated by the fact that activation of the last parent crystals coincides with the development of the avalanche. Thus, it should be assumed that the obtained mean number of parent crystals is underestimated.

With further increase of the parameter a , as the approximate construction for $a = 10$ and $a = 12$ shows, the edges of the curves drop, while the maximum increases; the shape of the curves approaches a bell-shaped one. The growth of the parameter a means an increase in the mean number of parent crystals. Consequently, in the symmetric case, the appearance of a large number of parent crystals leads to an increase in the probability of equality between right and left crystals in each experiment.

Thus, crystallization by means of multiplication can be characterized by curves ranging from cup-shaped to bell-shaped. The first of these corresponds to a process with a small number of avalanche-forming crystals, the second to crystallization with a large number of them. Various transitional forms are possible between them.

In conclusion, we note that the qualitative agreement of the theoretical and experimental curves in Fig. 1 confirms the correctness of the assumption made above concerning the exponential law of multiplication of epsomite crystals. Since this law is not connected with any specific features of dissymmetric crystals, it must, at least for processes of needle-like multiplication, have general significance.

Gorky Research
Physicotechnical Institute
at Gorky State University
named after N. I. Lobachevsky

Received
17 XII 1968

REFERENCES

1. É. D. Rogacheva, DAN, **165**, 1298 (1965).
2. R. E. A. Mason, R. F. Strickland-Constable, *Trans. Farad. Soc.*, **62**, 455 (1966).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.